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V. *On Super-acid and Sub-acid Salts.* By William Hyde Wollaston, M. D. Sec. R. S.

Read January 28, 1808.

IN the paper which has just been read to the Society, Dr. THOMSON has remarked, that oxalic acid unites to strontian as well as to potash in two different proportions, and that the quantity of acid combined with each of these bases in their super-oxalates, is just double of that which is saturated by the same quantity of base in their neutral compounds.

As I had observed the same law to prevail in various other instances of super-acid and sub-acid salts, I thought it not unlikely that this law might obtain generally in such compounds, and it was my design to have pursued the subject with the hope of discovering the cause to which so regular a relation might be ascribed.

But since the publication of Mr. DALTON's theory of chemical combination, as explained and illustrated by Dr. THOMSON,* the inquiry which I had designed appears to be superfluous, as all the facts that I had observed are but particular instances of the more general observation of Mr. DALTON, that in all cases the simple elements of bodies are disposed to unite atom to atom singly, or, if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms.

* THOMSON's Chemistry, 3d Edition, Vol. III. p. 425.

However, since those who are desirous of ascertaining the justness of this observation by experiment, may be deterred by the difficulties that we meet with in attempting to determine with precision the constitution of gaseous bodies, for the explanation of which Mr. DALTON's theory was first conceived, and since some persons may imagine that the results of former experiments on such bodies do not accord sufficiently to authorize the adoption of a new hypothesis, it may be worth while to describe a few experiments, each of which may be performed with the utmost facility, and each of which affords the most direct proof of the proportional redundance or deficiency of acid in the several salts employed.

Sub-carbonate of Potash.

Exp. 1. Sub-carbonate of potash recently prepared, is one instance of an alkali having one-half the quantity of acid necessary for its saturation, as may thus be satisfactorily proved.

Let two grains of fully saturated and well crystallized carbonate of potash be wrapped in a piece of thin paper, and passed up into an inverted tube filled with mercury, and let the gas be extricated from it by a sufficient quantity of muriatic acid, so that the space it occupies may be marked upon the tube.

Next, let four grains of the same carbonate be exposed for a short time to a red heat ; and it will be found to have parted with exactly half its gas ; for the gas extricated from it in the same apparatus will be found to occupy exactly the same space, as the quantity before obtained from two grains of fully saturated carbonate.

Sub-carbonate of Soda.

Exp. 2. A similar experiment may be made with a saturated carbonate of soda, and with the same result; for this also becomes a true semi-carbonate by being exposed for a short time to a red heat.

Super-sulphate of Potash.

By an experiment equally simple, super-sulphate of potash may be shewn to contain exactly twice as much acid as is necessary for the mere saturation of the alkali present.

Exp. 3. Let twenty grains of carbonate of potash (which would be more than neutralized by ten grains of sulphuric acid) be mixed with about twenty-five grains of that acid in a covered crucible of platina, or in a glass tube three quarters of an inch diameter, and five or six inches long.

By heating this mixture till it ceases to boil, and begins to appear slightly red hot, a part of the redundant acid will be expelled, and there will remain a determinate quantity forming super-sulphate of potash, which when dissolved in water will be very nearly neutralized by an addition of twenty grains more of the same carbonate of potash; but it is generally found very slightly acid, in consequence of the small quantity of sulphuric acid which remains in the vessel in a gaseous state at a red heat.

In the preceding experiments, the acids are made to assume a determinate proportion to their base, by heat which cannot destroy them. In those which follow, the proportion which a destructible acid shall assume cannot be regulated by the same means; but the constitution of its compounds previously formed, may nevertheless be proved with equal facility.

Super-oxalate of Potash.

Exp. 4. The common super-oxalate of potash is a salt that contains alkali sufficient to saturate exactly half of the acid present. Hence, if two equal quantities of salt of sorrel be taken, and if one of them be exposed to a red heat, the alkali which remains will be found exactly to saturate the redundant acid of the other portion.

In addition to the preceding compounds, selected as distinct examples of binacid salts, I have observed one remarkable instance of a more extended and general prevalence of the law under consideration ; for when the circumstances are such as to admit the union of a further quantity of oxalic acid with potash, I found a proportion, though different, yet analogous to the former, regularly to occur.

§. Quadroxalate of Potash.

In attempting to decompose the preceding super-oxalate by means of acids, it appeared that nitric or muriatic acids, are capable of taking only half the alkali, and that the salt which crystallizes after solution in either of these acids, has accordingly exactly four times as much acid as would saturate the alkali that remains.

Exp. 5. For the purpose of proving that the constitution of this compound has been rightly ascertained, the salt thus formed should be purified by a second crystallization in distilled water ; after which the alkali of thirty grains must be obtained by exposure to a red heat, in order to neutralize the redundant acid contained in ten grains of the same salt. The quantity of unburned salt contains alkali for one part out of

four of the acid present, and it requires the alkali of three equal quantities of the same salt to saturate the three remaining parts of acid.

The limit to the decomposition of super-oxalate of potash by the above acids, is analogous to that which occurs when sulphate of potash is decomposed by nitric acid; for in this case also, no quantity of that acid can take more than half the potash, and the remaining salt is converted into a definite super-sulphate, similar to that obtained by heat in the third experiment.

It is not improbable that many other changes in chemistry, supposed to be influenced by a general redundance of some one ingredient, may in fact be limited by a new order of affinities taking place at some definite proportion to be expressed by a simple multiple. And though the strong power of crystallizing in oxalic acid, renders the modifications of which its combinations are susceptible more distinct than those of other acids, it seems probable that a similar play of affinities will arise in solution, when other acids exceed their base in the same proportion.

In order to determine whether oxalic acid is capable of uniting to potash in a proportion intermediate between the double and quadruple quantity of acid, I neutralized forty-eight grains of carbonate of potash with thirty grains of oxalic acid, and added sixty grains more of acid, so that I had two parts of potash of twenty-four grains each, and six *equivalent* quantities of oxalic acid of fifteen grains each, in solution, ready to crystallize together, if disposed to unite, in the proportion of three to one; but the first portion of salt that crystallized, was the common binoxalate, or salt of sorrel, and a

portion selected from the after crystals (which differed very discernibly in their form) was found to contain the quadruple proportion of acid. Hence it is to be presumed, that if these salts could have been perfectly separated, it would have been found, that the two quantities of potash were equally divided, and combined in one instance with two, and in the other with the remaining four out of the six *equivalent* quantities of acid taken.

To account for this want of disposition to unite in the proportion of three to one by Mr. DALTON's theory, I apprehend he might consider the neutral salt as consisting of

	2 particles potash with 1 acid,
The binoxalate as 1 and 1, or 2	with 2,
The quadroxalate as 1 and 2, or 2	with 4,

in which cases the ratios which I have observed of the acids to each other in these salts would respectively obtain.

But an explanation, which admits the supposition of a double share of potash in the neutral salt, is not altogether satisfactory; and I am further inclined to think, that when our views are sufficiently extended, to enable us to reason with precision concerning the proportions of elementary atoms, we shall find the arithmetical relation alone will not be sufficient to explain their mutual action, and that we shall be obliged to acquire a geometrical conception of their relative arrangement in all the three dimensions of solid extension.

For instance, if we suppose the limit to the approach of particles to be the same in all directions, and hence their virtual extent to be spherical (which is the most simple hypothesis); in this case, when different sorts combine singly there is but one mode of union. If they unite in the proportion of

two to one, the two particles will naturally arrange themselves at opposite poles of that to which they unite. If there be three, they might be arranged with regularity, at the angles of an equilateral triangle in a great circle surrounding the single spherule; but in this arrangement, for want of similar matter at the poles of this circle, the equilibrium would be unstable, and would be liable to be deranged by the slightest force of adjacent combinations; but when the number of one set of particles exceeds in the proportion of four to one, then, on the contrary, a stable equilibrium may again take place, if the four particles are situated at the angles of the four equilateral triangles composing a regular tetrahedron.

But as this geometrical arrangement of the primary elements of matter is altogether conjectural, and must rely for its confirmation or rejection upon future inquiry, I am desirous that it should not be confounded with the results of the facts and observations related above, which are sufficiently distinct and satisfactory with respect to the existence of the law of simple multiples. It is perhaps too much to hope, that the geometrical arrangement of primary particles will ever be perfectly known; since even admitting that a very small number of these atoms combining together would have a tendency to arrange themselves in the manner I have imagined; yet, until it is ascertained how small a proportion the primary particles themselves bear to the interval between them, it may be supposed that surrounding combinations, although themselves analogous, might disturb that arrangement, and in that case, the effect of such interference must also be taken into the account, before any theory of chemical combination can be rendered complete.